Appendix L

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Synthesis of New Potential Molecular Wires and Molecular Alligator Clips.

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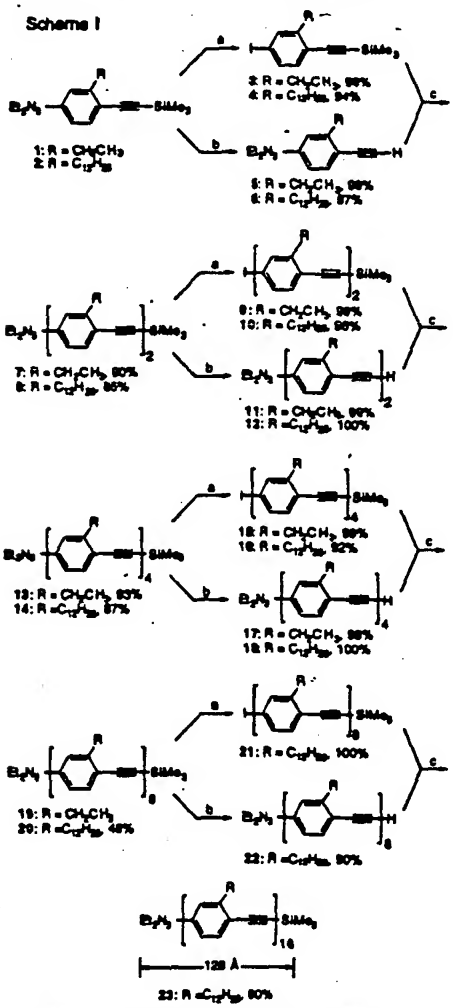
Recently, the construction of molecular electronic-based computational instruments has attracted much attention because the ultimate computational system would consist of logic devices that are ultra dense, ultra fast, and molecular-sized. The issue of electronic conduction based upon single or small packets of molecules has just recently been addressed by our research group.[1] The feasibility of molecular electronics, however, remains untested and is theoretically controversial.[2] Organic compounds have the potential to serve as molecular components of electronic devices.[3] As a prelude to the design of such devices, it is necessary to understand electrical conduction through single or small arrays of conjugated organic molecules that might ultimately serve as "molecular wires".[4]

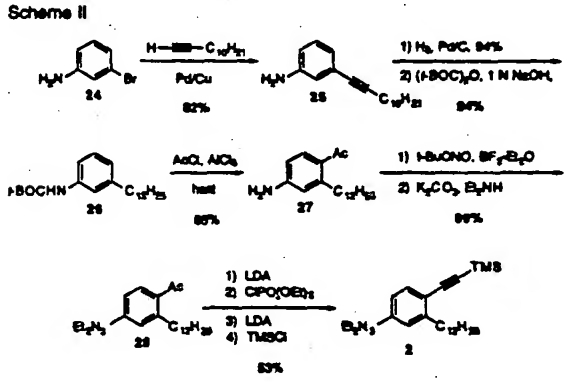
Scheme I



Reagents: a. MeI as solvent, 120°C in a screw cap tube. b. K_2CO_3, CH_2Cl_2, MeOH, 23°C to 65°C. c. $Pd(dba)_2$(5 mol %), CuI (10 mol %), PPh_3 (20 mol %), *i*-Pr_2NEt (4 eq.), THF, 23°C to 65°C.

Present state-of-the-art nanopatterning techniques allow lithographic probe assemblies to be engineered down to the 100 Å gap regime. In an attempt to assess the possibility of "molecular wire" conduction by spanning the 100 Å probe gaps with small packets of molecules, we previously synthesized a number of phenylene-alkynylene oligomers that remain in a near-linear conformation due to 1,4-phenylene-substitution patterns and alkyne linearity.[5a] Our approach to such a molecular framework involves the rapid iterative[6] divergent/convergent approach using, successively, the same three sets of reaction conditions (Scheme I). This linear arrangement should minimize undesired conformational movement during adhesion and testing between nanofabricated probes. The monomer, dimer, and tetramer, **1**, **7** and **13**, respectively, have been fully characterized. Tetramer **13**, as shown by computer generated molecular modeling techniques, is calculated to be 30 Å long from the aryl end to the acetylene end, and its corresponding octamer **19**, is calculated to be 60 Å long. Unfortunately, the insolubility of the octamer prevented us from proceeding beyond this point. We were, however, able to obtain a UV-visible spectrum and a direct exposure mass spectrum (MS) in order to provide partial evidence for the presence of the octamer **19**.

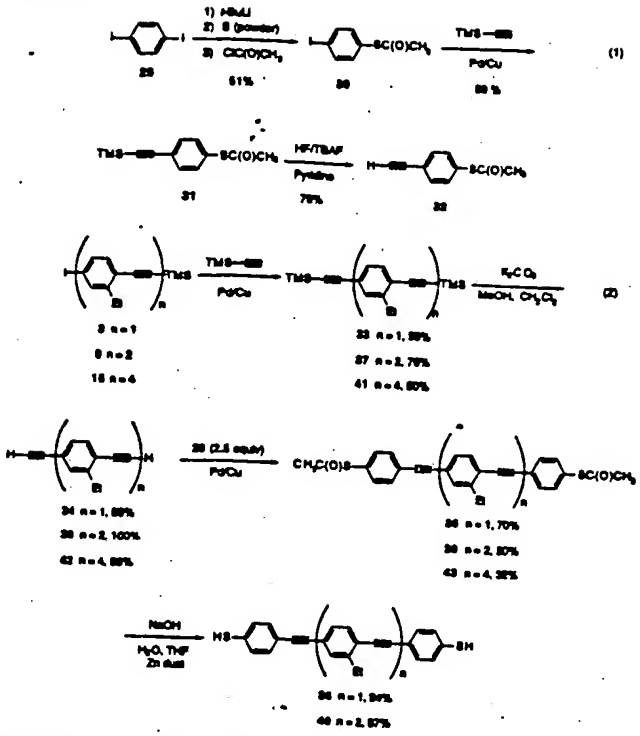
Scheme II



In an effort to insure the solubility of the longer linear rigid rod oligomers, we have prepared monomer **2** (Scheme II). As depicted, the ethyl group has been replaced with a dodecyl group. This modification should allow for easy purification and ensure oligomer solubility as it grows.[5b] We were delighted to discover that both the octamer **20** as well as the 16-mer **23** (Scheme I) were quite soluble and they could both be adequately spectroscopically characterized.

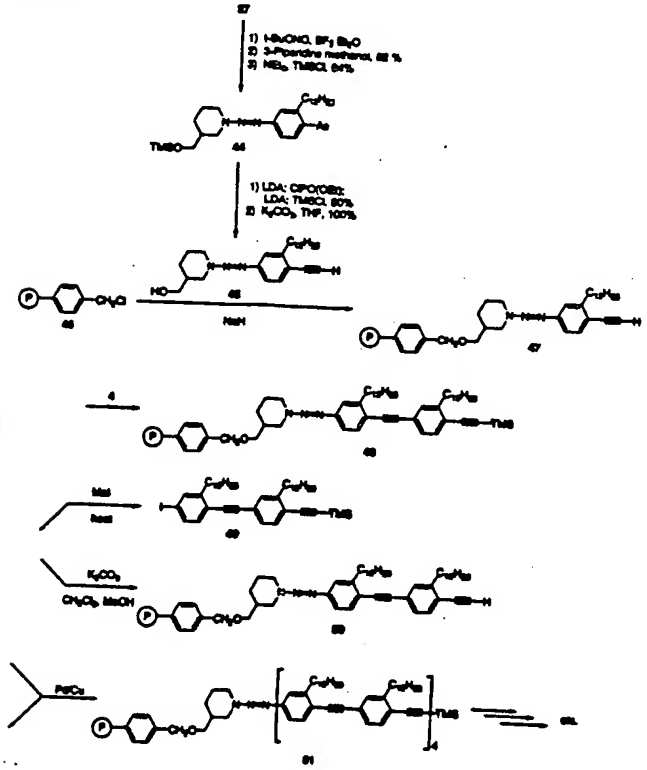
As outlined in Scheme III, we have developed the synthetic protocol for the synthesis (eq. 1) and attachment (eq. 2) of thiol and protected thiol end groups to the ends of our potential molecular wires. The thioacetates, upon hydrolysis, form thiols which upon exposure to gold surfaces form gold-thiolates.[7] Due to the oxidative instability of the thiols, we found that the optimal method for the deprotection and adhesion of these molecular systems may be via an *in situ* base-promoted acetate liberati n.[8] Various methods are currently under

Scheme III



investigation. We hope to use self-assembly methods to affix single or small packets of molecules between nanolithographically-derived probes or two STM tips.

Scheme IV



As shown earlier, we have demonstrated the synthesis of "molecular wires" by an iterative divergent/converg nt approach. We now plan to apply this same strategy using oligomers attached to a polymer support. This should significantly streamline the synthesis and isolation. Related solid phase approaches permit the preparation of oligopeptides and oligonucleotides in a commercially viable form,[9] and moreover, solid phase synthesis has recently been demonstrated to be useful for the construction of rigid rod oligomers.[10] Our proposed polymer-supported synthetic route is outlined in Scheme IV. The yields listed are for steps that have been conducted to date. Notice how the iterative divergent/convergent approach will be amenable to a polymer supported route.

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References and Notes

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